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Microfabrication of thermoelectric materials by silicon molding process

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Abstract

Thermoelectric microgenerators and microcoolers are becoming technologically important for microelectromechanical systems (MEMS), but the conventional cutting and assembling techniques have limitation in miniaturizing the dimensions of thermoelectric devices to the micrometer order. We have combined MEMS technology and materials processing into a novel process to manufacture thermoelectric micro-modules with densely aligned fine-scale and high-aspect-ratio P–N elements. Our process consists of the following major steps: (1) micromachining a silicon mold; (2) filling the mold with thermoelectric materials; (3) connecting P- and N-type elements and assembling the whole module. By using the present process, Bi–Sb–Te system thermoelectric elements of 300 μm height and 40 μm cross-sectional width can be fabricated successfully.

Keywords: Microfabrication; Thermoelectric device; Silicon molding; Materials micro-processing

1. Introduction

Thermoelectric materials can be used as solid-state devices that convert thermal energy from a temperature gradient into electrical energy, known as the "Seebeck effect", or generate a temperature gradient by the "Peltier effect" when electrons pass through the materials. Thermoelectric devices that work without any moving parts are virtually maintenance-free, and are environment-friendly because they do not use or generate gases of any kind. Thermoelectric devices can be used either in the Peltier mode for refrigeration or in the Seebeck mode for electrical power generation. One well-known example of thermoelectric applications is the radioisotope thermoelectric generators that provide electrical power to spacecrafts [1]. Recently, thermoelectric devices have received increasing attention because of their potential applications including microscale wireless energy sources [2–4] and accurate temperature controlling of infrared detectors and sophisticated electro-optic and telecommunication equipment [5,6]. Furthermore, Peltier devices also are expected to offer solutions to thermal management problems in microelectronic components and devices with high electrical power density. Such microelectronic applications require us to remarkably reduce the sizes of the thermoelectric devices. A typical thermoelectric module consists of a few couples of P- and N-type elements that are connected electrically in series.

Conventionally, thermoelectric elements are prepared by mechanically dicing thermoelectric single crystals or sintered materials. Since most thermoelectric materials are mechanically weak, conventional mechanical machining has its limitation to miniaturization. Therefore, increasing attention has been paid on the development of novel manufacturing technology of thermoelectric microdevices. For example, two watch's makers in Japan have successfully developed thermoelectric microgenerators that produce electrical energy to run a wristwatch [7,8]. Fleurial and coworkers [9] successfully fabricated much smaller elements (20 μm in diameter and 50 μm high) using an electrochemical deposition process to develop thick-film thermoelectric microcoolers. Recently, we have proposed a silicon molding process, by which alternately aligned P- and N-type thermoelectric elements with microscale cross-section and high aspect ratio can be built in a single micromachined silicon mold [10].

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This paper introduces the full details of the silicon molding process and presents some new experimental results about the microfabrication of thermoelectric materials.

2. Fabrication process and experimental details

As shown in Fig. 1, our process mainly consists of the three major steps: (1) micromachining a silicon mold; (2) filling the mold with thermoelectric materials; (3) connecting P- and N-type elements and assembling the whole module. A similar silicon molding process has been successfully used to microfabricate piezoelectric ceramic microrod arrays [11,12] for ultrasonic micro-transducers and SiC ceramic microrotors [13] for microscale gas turbines.

The silicon mold was micromachined by using photolithography and reactive ion etching (RIE) techniques according to the following procedures. First, one surface of a silicon wafer was spin-coated with a positive photoresist (AZ P4400) film, which was then subjected to optical patterning. A set of vertical holes was produced on one side of the wafer by deep RIE using a multiplex inductively-coupled-plasma (ICP) etcher (Surface Technology Systems, Multiplex ICP-RIE System). The same procedures were repeated on another side so that equal numbers of aligned holes were formed on both sides of the Si wafer.

Although the present silicon molding process can be used for the microfabrication of many thermoelectric materials including metallic or semi-metallic compounds and ceramics, the first try was focused on Bi–Sb–Te alloys, because which is the state-of-the-art thermoelectric materials used in some commercialized thermoelectric devices. Commercially available Bi–Sb–Te alloy (P-type: $(Bi_{0.25}Sb_{0.75})_2(Te_{0.93}Se_{0.07})_3$; N-type: $(Bi_2Te_3)_{0.975}(Bi_2Se_3)_{0.025}+$ 0.05 mass% SbI_3) ingots were used as the starting material, which were crushed to powders by an automatic mill with a mortar and a ball made of agate.

A novel method like die-casting was used to fill the deep and narrow holes with Bi–Sb–Te thermoelectric alloys. As shown in Fig. 2, the Si mold was set in a glass container like as a dish, with P- and N-alloy powders being on and under the Si mold, then vacuum-encapsulated to a glass tube. The encapsulated sample was placed in a BN crucible and heated in an electric furnace in a pressurized atmosphere of Ar gas. The heating and pressurizing schedules are shown in Fig. 3. The temperature was first increased to 883 K at a

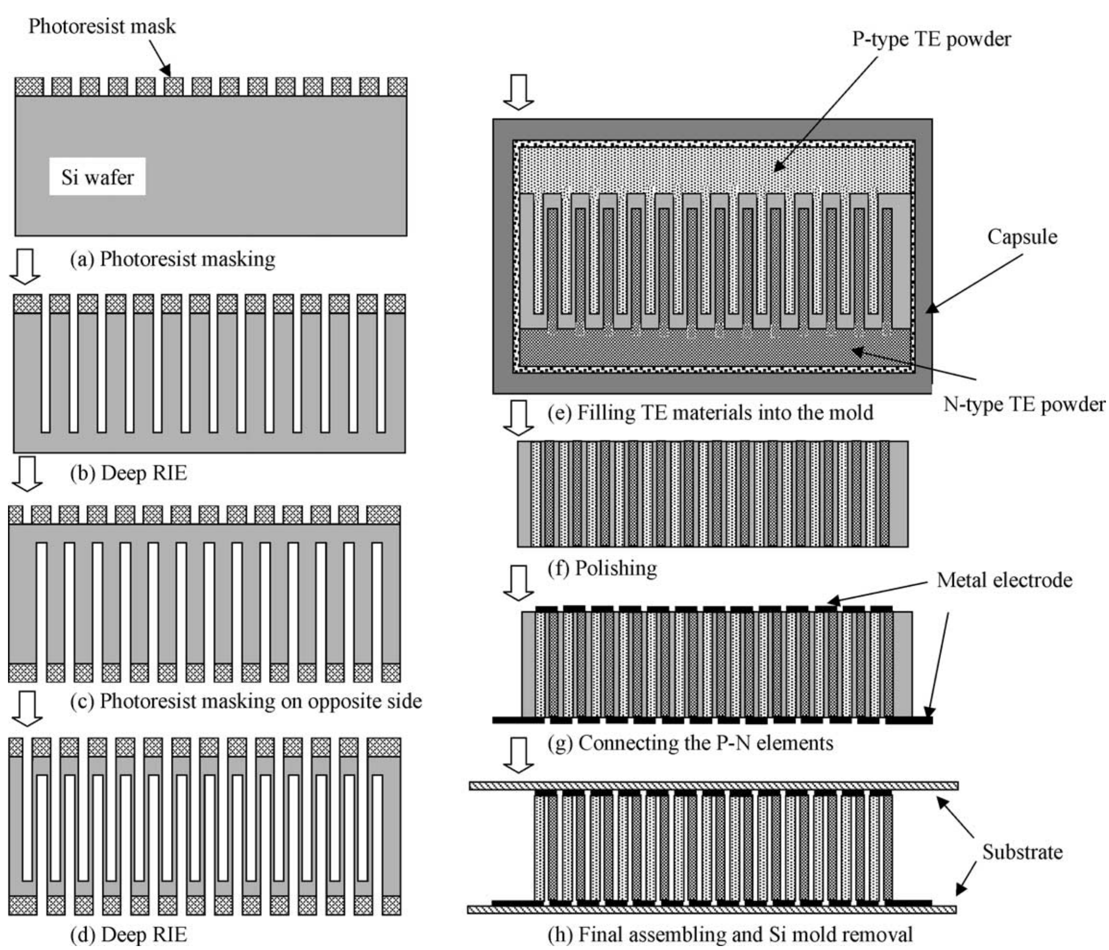

Fig. 1. Schematic flow chart of the proposed process for fabrication of thermoelectric micro-modules.

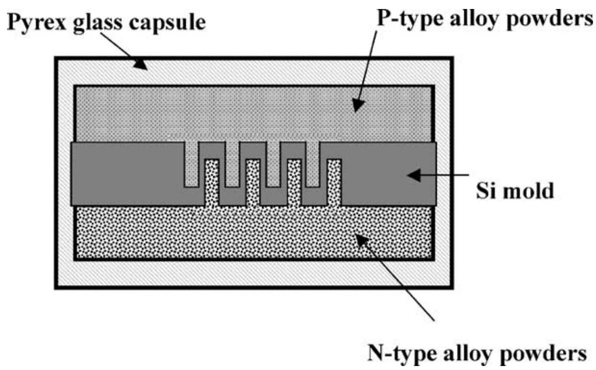

Fig. 2. Illustration showing the arrangement of Si mold and thermoelectric alloy powders, which are to be squeezed into the hole array of Si mold.

heating rate of 10 K/min, and then the temperature and the Ar pressure were simultaneously raised to 973 K and 1 MPa, respectively, within 30 min. Because the Pyrex glass capsule become relatively softened at temperatures near 973 K, the gas pressure can be transmitted to the melted Bi–Sb–Te alloys, whose melting points are 879 and 861 K, respectively, for P- and N-type compositions. As a result, the Bi–Sb–Te melts are squeezed into the Si mold. Then, the temperature was decreased at a rate of 10 K/min and the pressure was reduced accordingly. The mold filled with the thermoelectric alloys was taken out by removing the squashed glass capsule and the materials remaining on the mold surface.

Finally, the surfaces of the silicon mold containing the thermoelectric elements are polished to a certain depth, where the bottom end of the elements filled from the opposite surface just appeared on the polished surfaces. After that, the element ends will be connected to form thermocouples by using photolithography and metal deposition techniques, and then fixed onto two substrates with high thermal conductivity (AlN or SiC). The remaining silicon between P- and N-type elements can be released finally by dry etching with XeF_2 gas.

Scanning electron microscopy (SEM) was used to observe the microstructure of the filled thermoelectric elements. The compositions of the filled materials and the boundary between the filled materials and silicon mold were analyzed using an electron probe microanalyzer (EPMA).

3. Results and discussion

The scanning electron micrograph (SEM) of one Si mold micromachined by the above process is shown in Fig. 4. This Si mold was made from a 20 mm^2 piece of 400 μm thick Si wafer, and the central portion of 10 mm^2 was micromachined to contain 10,000 holes of 300 μm deep and 40 μm^2 on each side. Such deep and narrow holes were perfectly produced by the deep RIE process operated with the optimized condition parameters. Although we confirmed that it was possible to "drill" smaller and deeper holes by the above process, the Si mold shown in Fig. 4 was used as the first version to manufacture a TE micro-module with 10,000 P–N couples.

Fig. 5 shows the SEM micrograph of the polished surface of the filled silicon mold. Although the heating and pressurizing schedule was not necessarily optimal, the deep and narrow holes were filled successfully with the Bi–Sb–Te alloys. Besides the pressure transmitted through the glass capsule, the capillary effect also enhanced the filling of the molten Bi–Sb–Te alloys.

Fig. 6 shows the EPMA analysis maps of the side cross-section of one single P-type element in the Si mold. The Bi and Si distributions between the two red lines across the element width direction were measured, and no distinguishable interdiffusion was observed between the filled materials and the silicon mold wall. This fact is acceptable because the temperature was considerably low.

Fig. 7 shows a portion of the side cross-section of the filled Si mold to display that P- and N-type Bi–Sb–Te alloys were successfully pressed into the hole arrays from both side of the Si mold. Note that some elements were broken

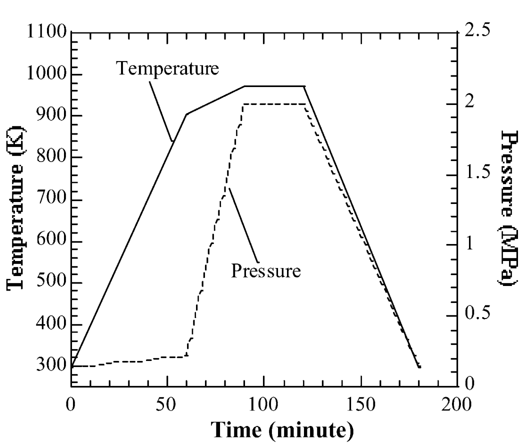

Fig. 3. Heating and pressurizing program for filling P-type Bi–Sb–Te alloy into Si molds.

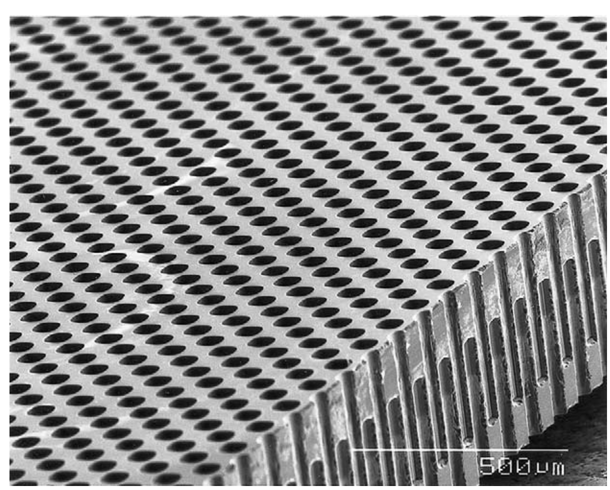

Fig. 4. SEM micrographs of a micromachined silicon mold for microfabricating thermoelectric devices.

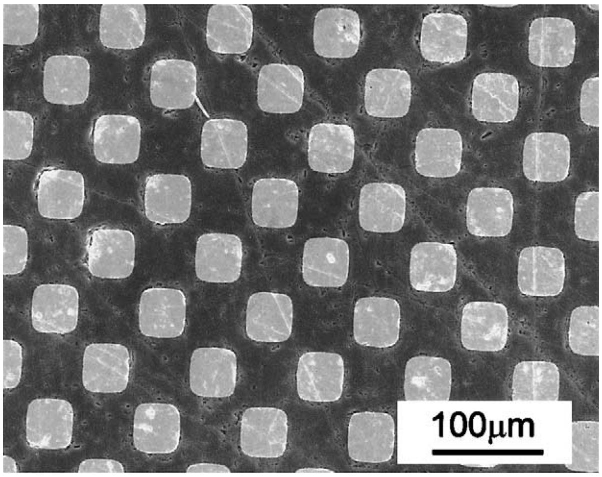

Fig. 5. SEM micrograph of the polished surface of the silicon mold with the P-type Bi–Sb–Te alloy elements filled inside.

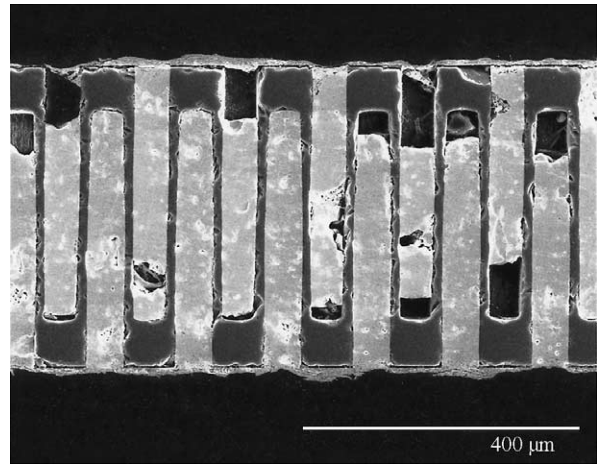

Fig. 7. SEM micrograph of a portion of side section of a mold filled with P- and N-types of Bi–Sb–Te alloys.

during the sample preparation by conventional mechanical polishing, although the holes were actually completely filled. However, the filled Si mold was deformed and some cracks formed in it after the pressurized casting process, probably due to the non-uniform deformation of the glass capsule. More experiments are in progress to overcome this problem by changing the glass-encapsulating method.

The above sample was placed in a special chamber and exposed to XeF_2 gas to remove the silicon mold. Although this step should be after the assembling of a whole thermoelectric module, the experiment was done here to show that the silicon phase between the filled elements could be removed selectively. As shown in Fig. 8, the silicon mold was selectively removed by XeF_2 gas, and the thermoelectric elements remained standing well. The protuberant height was about 60 µm after the gas etching for 60 min; however, note that the total height of the elements is as long as 300 µm. According to the authors' knowledge, such long and fine thermoelectric elements were fabricated for the first time in the present study. In addition, it is not difficult to further reduce the dimensions of the elements by the present process.

A simple calculation is made below to estimate the thermoelectric performance of the thermoelectric modules with above microfabricated elements. The output electrical voltage (V) of a thermoelectric module is proportional to the numbers (m) of P–N thermocouples and the effective temperature gradient (ΔT) across the module thickness, as shown by the following equation:

$$V = m\alpha_e \, \Delta T, \tag{1}$$

where α_e is the effective thermoelectric power, equaling to 400 µV/K for the Bi–Sb–Te system thermoelectric alloys. The temperature gradient, which increases the voltage proportionally, is determined by the effective thermal conductivity of a thermoelectric module. Because the thermal conductivity of Bi–Sb–Te alloy is as low as 1.5 W/mK, a fairly steep temperature gradient may be easily generated

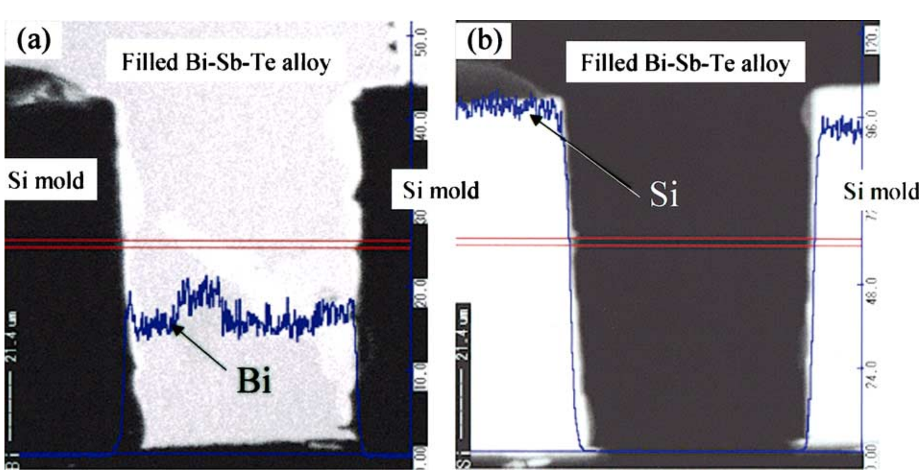

Fig. 6. EPMA maps of the side cross-section of a filled P-type element in the Si mold. Note that the blue lines in (a) and (b) are Bi and Si distributions, respectively, in the area between the two red lines.

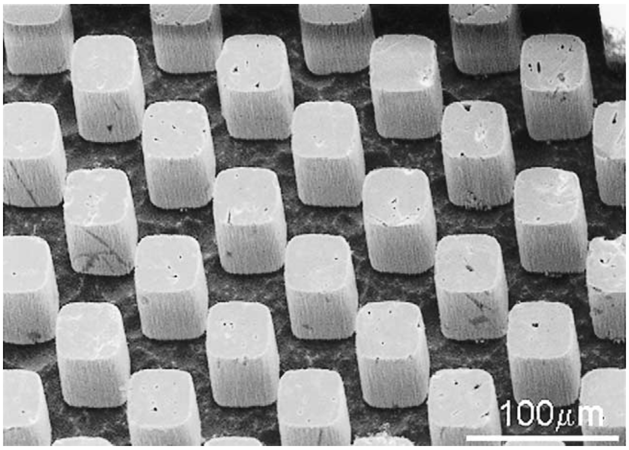

Fig. 8. SEM micrograph of the P-type Bi–Sb–Te element array obtained by selectively removing silicon phases between the elements using the XeF_2 gas etching method.

across the module's thickness. For example, if the present module is subjected to a heat flux as low as 25 kW/m^2, the temperature difference will be 5 K between the ends of 300 μm elements high. Under such a temperature gradient, our thermoelectric microdevices, which have 10,000 thermocouples ($m = 10{,}000$) over a 100 mm^2 area, are estimated to generate a voltage as high as 20 V.

4. Summary

A novel micro-materials process using micromachined silicon molds has been proposed to fabricate thermoelectric micro-modules with extremely high density of fine and high P–N elements. Silicon molds with 10,000 holes of 300 μm deep and 40 μm^2 in a 100 mm^2 area were successfully prepared, and Bi–Sb–Te alloy element arrays with dimensions equal to the holes were fabricated using the micromachined Si mold. Miniaturization process of thermoelectric devices has dual meanings: reducing the whole size and increasing packing density of thermoelectric elements. The present process based on MEMS technology has opened up a new way to manufacture thermoelectric microdevices with densely aligned microscale cross-section and high-aspect-ratio thermoelectric elements.

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Biographies

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Ryuzo Watanabe received his BE, ME, and Dr E degrees in metallurgy from Tohoku University in 1964, 1966 and 1977, respectively. He was an assistant professor from 1996 to 1978, was an associate professor from 1978 to 1986, is currently a professor all in the Department of Materials Processing, Tohoku University, Japan. He was a visiting professor at Max-Planck-Institute for Metals Research, Germany in 1986. His research interests include functionally graded materials, sintering mechanisms, mechanisms of mechanical alloying and properties of sintered composites.